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(54) Title: UV/EB CURABLE BUTYL COPOLYMERS FOR COATING APPLICATIONS

(57) Abstract

A radiation reactive functionalized polymer comprising an isoolefin having about 4 to about 7 carbon atoms and a para-alkylstyrene, wherein a radiation reactive functional group is attached to the para-alkyl group of the para-alkylstyrene. The polymer has a substantially homogeneous compositional distribution and may be utilized in lithographic and coating applications. Also disclosed are radiation curable pressure sensitive adhesives comprising the functionalized polymer and a tackifier.

CLAIMS:

1. A radiation-curable coating composition, comprising:
   (a) a radiation-crosslinkable functionalized polymer of an isoolefin of 4 to 7 carbon atoms and para-alkylstyrene comonomer, said functionalized polymer having substantially homogeneous compositional distribution wherein the comonomer is functionalized with a radiation-reactive group at the para-alkyl group of the para-alkylstyrene; and
   (b) a tackifier resin.

2. The coating composition of claim 1, wherein said functionalized polymer has a number average molecular weight of at least about 5000.

3. The coating composition of claim 2, wherein said functionalized polymer has a number average molecular weight of between about 5000 and 500,000.

4. The coating composition of claim 1, wherein said functionalized polymer has a ratio of weight average molecular weight to number average molecular weight of less than about 6.

5. The coating composition of claim 1, wherein at least about 95 weight percent of said functionalized polymer has a para-alkylstyrene content within about 10 weight percent of the average para-alkylstyrene content for said functionalized polymer.

6. The coating composition of claim 1, wherein said isoolefin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

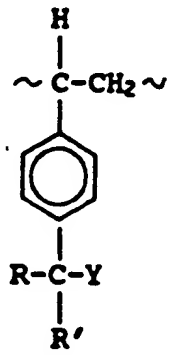
7. The coating composition of claim 6, wherein said functionalized polymer has a number average molecular weight greater than about 5000.

8. The coating composition of claim 7, wherein said functionalized polymer has a ratio of weight average molecular weight to number average molecular weight of less than about 6.

9. The coating composition of claim 1, wherein said isoolefin and said para-alkylstyrene are present in said functionalized polymer in amounts such that said isoolefin comprises from about 10 to 99.5 percent by weight of said polymer and said para-alkylstyrene comprises from about 0.5 to 90 percent by weight of said functionalized polymer.

10. The coating composition of claim 9, wherein said isoolefin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

11. The coating composition of claim 1, wherein said copolymer includes said para-alkylstyrene as



wherein R and R′ are independently selected from the group consisting of hydrogen, alkyl, and primary and secondary alkyl halide radicals and Y comprises a mixture of hydrogen and radiation-reactive functionality.

12. The coating composition of claim 11, wherein R and R′ are independently selected from the group consisting of hydrogen, C_1 to C_5 alkyl and C_1 to C_5 primary and secondary alkyl halide.

13. The coating composition of claim 11, wherein said radiation-reactive functionality comprises a nucleophillically substituted photoinitiator selected from the group consisting of benzophenone, 4-chlorobenzophenone, 4-hydroxybenzophenone, benzoquinone, naphthaquinone, anthraquinone, 2-chloroanthraquinone, benzylidene acetophenone, acetophenone, propiophenone, cyclopropyl phenyl ketone, benzaldehyde, β-napthylphenyl ketone, β-napthaldehyde, β-acetonaphthone, 2,3-pentanedione, benzil, fluorenone, benzanthrone, Michler's ketone, bis(parahydroxybenzylidene)acetone, benzoin, deoxybenzoin, and chlorodeoxybenzoin.

14. The coating composition of claim 11, wherein said radiation-reactive functionality comprises nucleophilically substituted thioxanthone.

15. The coating composition of claim 11, wherein said radiation-reactive functionality comprises a nucleophilically substituted photoinitiator selected from N,N-disubstituted dithiocarbamic acid and esters and salts thereof.

16. The coating composition of claim 11, wherein said radiation-reactive functionality comprises a nucleophilically substituted photoinitiator selected from tung oil acid and esters and salts thereof.

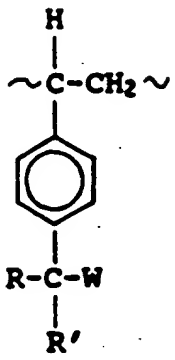
17. The coating composition of claim 11, wherein said radiation-reactive functionality comprises photoinitiators selected from the group consisting of benzoic acid, cinnamic acid, m-nitrocinnamic acid, p-chlorocinnamic acid, p-methoxycinnamic acid, chalcone acrylic acid, p-phenylenebis(acrylic acid) p-azidobenzoic acid, p-sulfonazidebenzoic acid, α-cyanocinnamic acid, cinnamylideneacetic acid, cinnamylidenemalonic acid, α-cyanocinnamylideneacetic acid, β-(1)-naphthylacrylic acid, β-(2)-furfurylacrylic acid, α-cyano-β-(2)-thienylacrylic acid, β-(1) naphthylacrylic acid, β-(9)-anthrylacrylic acid and esters and salts thereof.

18. The coating composition of claim 1, wherein said polymer comprises from about 5 to about 95 parts by weight of the composition and said tackifier comprises from about 5 to about 95 parts by weight of the composition, wherein parts by weight of the polymer and the tackifier total 100.

19. The coating composition of claim 1, wherein said polymer comprises from about 30 to about 70 parts by weight of the composition and said tackifier comprises from about 30 to about 70 parts by weight of the composition, wherein parts by weight of the polymer and the tackifier total 100.

20. The coating composition of claim 1, wherein said copolymer comprises from about 10 to about 99.5 weight percent of said isoolefins and from about 0.5 to about 90 weight percent of said para-alkylstyrene.

21. The coating composition of claim 20, wherein said para-alkylstyrene is included in said polymer as:



wherein R and R′ are independently selected from hydrogen, alkyl and primary and secondary alkyl halide, and W is selected from hydrogen, X, Y and Z, wherein X is chlorine or bromine, Y is a radiation-reactive functional group, and Z is a non-radiation-reactive functional group containing oxygen, sulfur, silicon, nitrogen, carbon or metal selected from sodium potassium, lithium and magnesium, wherein said para-alkylstyrene wherein W is hydrogen comprises from about 0.5 to about 99.5 percent by weight of said polymer, said para-alkylstyrene, wherein W is Y comprises from about 0.5 to about 55 percent by weight of said polymer, said para-alkylstyrene, wherein W is X comprises from 0 to 55 percent by weight of said polymer, and said para-alkylstyrene wherein W is Z comprises from 0 to 55 percent by weight of said polymer, said polymer having a number average molecular weight above about 5000.

22. The coating composition of claim 21, wherein said para-alkylstyrene wherein W is hydrogen comprises from about 1 to about 20 percent by weight of said polymer, said para-alkylstyrene wherein W is Y comprises from about 0.5 to about 20 percent by weight of said polymer, said para-alkylstyrene wherein W is X comprises less than about 20 percent by weight of said polymer, and said para-alkylstyrene wherein W is Z comprises from 0 to about 20 percent by weight of said polymer, said polymer having a number average molecular weight from about 5000 to about 500,000 and a ratio of weight average molecular weight to average molecular weight less than about 6.

23. The coating composition of claim 21, wherein said para-alkylstyrene wherein W is hydrogen comprises from about 2 to about 10 percent by weight of said polymer, said para-alkylstyrene wherein W is Y comprises from about 0.5 to about 15 percent by weight of said polymer, said para-alkylstyrene wherein W is X comprises less than about 15 percent by weight of said polymer, and said para-alkylstyrene wherein W is Z comprises from 0 to about 15 percent by weight of said polymer, said polymer having a number average molecular weight from about 5000 to about 500,000 and a ratio of weight average molecular weight to average molecular weight less than about 6.

24. The coating composition of claim 21, wherein said para-alkylstyrene wherein W is Y comprises from about 1 to about 7 percent by weight of said polymer, abd said para-alkylstyrene wherein W is X comprises less than about 1 percent by weight of said polymer, said polymer having a number average molecular weight from about 5000 to about 500,000 and a ratio of weight average molecular weight to average molecular weight less than about 6.

25. The coating composition of claim 21, wherein said polymer is essentially free of said para-alkylstyrene wherein W is X.

26. The coating composition of claim 22, wherein said polymer comprises less than about 1 percent by weight of said para-alkylstyrene wherein W is X.

27. A process for producing a radiation-crosslinkable functionalized polymer, comprising reacting:

(a) in a nucleophilic substitution reaction, a halogenated polymer comprising an isoolefin of 4 to 7 carbon atoms and a para-alkylstyrene comonomer, said polymer having a substantially homogeneous compositional distribution and essentially free of halogen atoms in the polymer backbone and also in the aromatic rings, said halogen atoms being substantially alkylhalide attached to the pendant para-alkylstyrene and primarily alkylmonohalide; with

(b) a nucleophilic reagent comprising a radiation reactive nucleophile.

28. The process of claim 27, further comprising the preliminary steps of reacting said isoolefin and said para-alkylstyrene in a polymerization reactor under polymerization conditions in the presence of a diluent and a Lewis Acid catalyst, maintaining said polymerization reactor substantially free of impurities which can complex with said catalyst or copolymerize with said isoolefin or said para-alkylstyrene to obtain a precursor copolymer, and contacting said precursor copolymer with a halogen in the presence of a free radical initiator to obtain said halogenated polymer.

29. The process of claim 27, wherein said isoolefin comprises isobutene and said para-alkylstyrene comprises para-methylstyrene.

30. The process of claim 27, wherein said halogen comprises bromine.

31. The process of claim 27, wherein said radiation reactive nucleophile comprises a nucleophilically substituted photoinitiator selected from the group consisting of benzophenone, 4-chlorobenzophenone, 4-hydroxybenzophenone, benzoquinone, naphthaquinone, anthraquinone, 2-chloroanthraquinone, benzylidene aceto-phenone, acetophenone, propiophenone, cyclopropyl phenyl ketone, benzaldehyde, β-napthylphenyl ketone, β-napthaldehyde, β-acetonaphthone, 2,3-pentanedione, benzil, fluorenone, benzanthrone, Michler's ketone, bis(parahydroxybenzylidene)acetone, benzoin, deoxybenzoin, and chlorodeoxybenzoin.

32. The process of claim 27, wherein said radiation reactive nucleophile comprises nucleophilically substituted thioxanthone photoinitiator.

33. The process of claim 27, wherein said radiation reactive nucleophile comprises a nucleophilically substituted photoinitiator selected from N,N-disubstituted dithiocarbamic acid and esters and salts thereof.

34. The process of claim 27, wherein said radiation reactive nucleophile comprises a nucleophilically substituted photoinitiator selected from tung oil acid and esters and salts thereof.

35. The process of claim 27, wherein said radiation reactive nucleophile comprises a nucleophilically substituted photoinitiator selected from benzoic acid, cinnamic acid, m-nitrocinnamic acid, p-chlorocinnamic acid, p-methoxycinnamic acid, chalcone acrylic acid, p-phenylenebis(acrylic acid) p-azidobenzoic acid, p-sulfonazidebenzoic acid, α-cyanocinnamic acid, cinnamylideneacetic acid, cinnamylidenemalonic acid, α-cyanocinnamylidene-acetic acid, β-(1)-naphthylacrylic acid, β-(2)-furfuryl-acrylic acid, α-cyano-β-(2)-thienylacrylic acid, β-(1) naphthylacrylic acid, β-(9)-anthrylacrylic acid and esters and salts thereof.

36. A coated article having adhered to at least a portion of a surface thereof, the radiation curable coating composition of claim 1.

37. The article of claim 36, wherein said surface is coated with a hot melt of said coating composition.

38. The article of claim 36, wherein said coating composition is crosslinked by exposure to electromagnetic radiation.

39. A method for making a coated article, comprising the steps of:

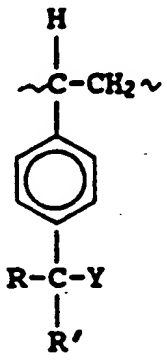
(a) coating at least a portion of a surface of the article with the coating composition of claim 1;

(b) exposing said surface to electromagnetic radiation to crosslink the coating composition.

40. The method of claim 39, wherein said surface is coated with a hot melt of said coating composition.

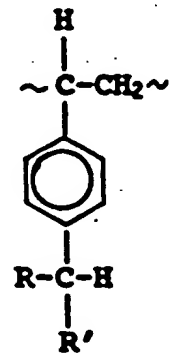
41. The method of claim 39, wherein said crosslinking radiation comprises electron beam or gamma radiation.

42. A radiation curable copolymer, comprising an isoolefin of 4 to 7 carbon atoms randomly polymerized with a para-alkylstyrene comonomer, wherein the para-alkylstyrene is included as

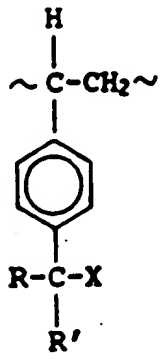


wherein R and R′ are independently selected from the group consisting of hydrogen, alkyl and primary and secondary alkyl halides, and Y is a radiation-reactive functional group added by nucleophilic substitution of a photoinitiator compound selected from one or more of aromatic aldehydes and ketones, alkoxy and acyl-substituted aromatics, hetero aromatics, fused ring polycyclic aromatics, dithiocarbamates, unsaturated fatty acids, aromatic carboxylic acids, nitroaromatics, dye compounds, azides, diazonium salts and combinations thereof.

43. The copolymer of claim 42, wherein said para-alkylstyrene is further included as

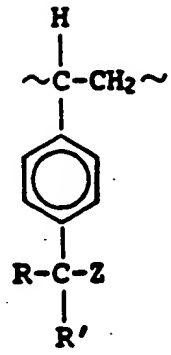


44. The copolymer of claim 42, wherein said para-alkylstyrene is further included as



wherein X is halogen.

45. The copolymer of claim 42, wherein said para-alkylstyrene is further included as



wherein Z is a non-radiation-reactive functional group containing oxygen, sulfur, silicon, nitrogen, carbon, phosphorus or a metal selected from sodium, potassium, lithium, and magnesium.

46. The copolymer of claim 42, wherein said photoinitiator comprises a nucleophilically substituted photoinitiator selected from the group consisting of benzophenone, 4-chlorobenzophenone, 4-hydroxybenzophenone, benzoquinone, naphthaquinone, anthraquinone, 2-chloroanthraquinone, benzylidene aceto-phenone, acetophenone, propiophenone, cyclopropyl phenyl ketone, benzaldehyde, β-napthylphenyl ketone, β-napthaldehyde, β-acetonaphthone, 2,3-pentanedione, benzil, fluorenone, benzanthrone, Michler's ketone, bis(parahydroxybenzylidene)acetone, benzoin, deoxybenzoin, and chlorodeoxybenzoin.

47. The copolymer of claim 42, wherein said photoinitiator comprises nucleophilically substituted thioxanthone.

48. The copolymer of claim 42, wherein said photoinitiator comprises a nucleophilically substituted photoinitiator selected from N,N-disubstituted dithiocarbamic acid and esters and salts thereof.

49. The copolymer of claim 42, wherein said photoinitiator comprises a nucleophilically substituted photoinitiator selected from tung oil acid and esters and salts thereof.

50. The copolymer of claim 42, wherein said photoinitiator comprises photoinitiators selected from the group consisting of benzoic acid, cinnamic acid, m-nitrocinnamic acid, p-chlorocinnamic acid, p-methoxycinnamic acid, chalcone acrylic acid, p-phenylenebis(acrylic acid) p-azidobenzoic acid, p-sulfonazidebenzoic acid, α-cyanocinnamic acid, cinnamylideneacetic acid, cinnamylidenemalonic acid, α-cyanocinnamylideneacetic acid, β-(1)-naphthyl-acrylic acid, β-(2)-furfurylacrylic acid, α-cyano-β-(2)-thienylacrylic acid, β-(1) naphthylacrylic acid, β-(9)-anthrylacrylic acid and esters and salts thereof.

51. A coated article, comprising an article having adhered to at least a portion of a surface thereof, the radiation-curable copolymer of claim 42.

52. The article of claim 51, wherein said surface is coated with a hot melt of the copolymer.

53. The article of claim 51, wherein said copolymer is crosslinked by exposure to electromagnetic radiation.

54. A method for making a coated article, comprising the steps of:

(a) coating at least a portion of a surface of the article with the copolymer of claim 42;

(b) exposing said surface to electromagnetic radiation to crosslink the copolymer.

55. The method of claim 54, wherein said coating comprises a hot melt or solvent application.

56. The method of claim 54, wherein said crosslinking radiation comprises ultraviolet, electron beam or gamma radiation.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/09653

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 F 2/54, 210/10, C 09 D 125/04, G 03 F 7/027
C 08 L 23/22

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 F; C 08 L; C 09 D; G 03 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

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* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13th April 1992	29.04.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Nicole De Bie

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 3948868 (KENNETH W. POWERS) 6 April 1976, see column 3, line 15; claim 1	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 91/09653

SA 55792

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/02/92
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US-A- 3948868	06/04/76	NONE		

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/00661

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 107 (C-341), 22 April 1986 & JP,A,60 237039 (NIPPON YUSHI KK), 25 November 1985, see abstract	1-29
Y	CHEMICAL ABSTRACTS, vol. 82, no. 10, 10 March 1975 Columbus, Ohio, US; abstract no. 59971p, KARMANOVA ET AL: "light stabilizers of daytime fluorescent paints" page 147; XP002002978 see abstract & STSINTILL. ORG. LYUMINOFORY, 1972, pages 151-156,	1-29
Y	CHEMICAL ABSTRACTS, vol. 112, no. 9, 26 February 1990 Columbus, Ohio, US; abstract no. 76077g, ZHANG,JINGWEN ET AL: "relation between solvating power and dielectric constants for the dehydration of tertiary alcohol to alkenes" page 699; XP002002979 see abstract & GAODENG XUEXIAO HUAXUE XUEBAO, vol. 10, no. 8, 1989, pages 872-874,	30-35
A	DATABASE WPI Section Ch, Week 8724 Derwent Publications Ltd., London, GB; Class A89, AN 87-167588 XP002002980 & JP,A,62 100 557 (MITSUBISHI DENKI KK), 11 May 1987 see abstract	1-29
A	EP,A,0 262 533 (BASF AG) 6 April 1988 see abstract	30-35

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int ional Application No
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